THE JOHNS HOPKINS UNIVERSITY

DEPARTMENT OF PHYSICS

LASER RAMAN SCATTERING STUDIES OF CRYSTALS

SEMIANNUAL PROGRESS REPORT
CONTRACT NO. NONR-4010(06)
ARPA ORDER NO. 306-63
PROGRAM CODE 3730

AUG. 1, 1967

Baltimore, Maryland 21218

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Report Period: 16 December 1966 - 15 June 1967
Contract Term: 16 June 1963 - 15 June 1968

Prepared by:

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This research is part of PROJECT DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, Department of Defense and the Office of Naval Research.

Project Personnel

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PUBLICATIONS

1) "Visual Observation of Ferroelectric Domains in TGS", Stephen M. Shapiro, Robert W. Gammon and Herman Z. Cummins, Applied Physics Letters 10, 113 (1967).

2) "Temperature Dependent Raman Spectrum of Strontium Titanate", D. C. O'Shea, R. V. Kolluri and H. Z. Cummins Solid State Communications 5, 241 (1967).

3) [Submitted to Physical Review Letters] "Raman Scattering Study of the Alpha-Beta Phase Transition in Quartz", Stephen M. Shapiro, Donald C. O'Shea and Herman Z. Cummins.

Fiscal Data (through June 30, 1967)

Total Appropriation	$143,409.48
Total Expenditures	114,077.41
Estimated Unpaid Commitments	2,000.00
Estimated Balance	$ 27,332.07

ABSTRACT

Temperature dependent Raman spectroscopy of quartz has revealed the existence of a new optical lattice vibration mode which appears to play a fundamental role in the alpha-beta phase transition.

Continued temperature dependent Raman measurements of Strontium Titanate have also disclosed a new "moving" component in the spectrum. Additional measurements have also shown that the three sharp Raman lines which are present at all temperatures below the 110° K. cubic to tetragonal transition probably arise from local breaking of the translational symmetry by inhomogeneous strain within the domain walls. Intensity vs. temperature measurements of the strong component at 78 cm^{-1} (room temperature value) have failed to confirm our earlier conclusion that part of the room temperature Raman spectrum of Strontium Titanate is of first order.

Preliminary Raman measurements have been performed on KDP, and have failed to produce conclusive evidence for an anticipated "soft" mode which was predicted by Cochran.

CONTENTS

I. INSTRUMENTATION

The Laser Raman Spectrograph currently in use in this laboratory includes the following components:

A. Raman Source

All work reported in the following sections was performed using a Spectra-Physics model 125 He-Ne laser with approximately 80 mw output at 6328 Å. We are currently awaiting delivery of a Spectra-Physics model 140 argon ion induction laser which will provide approximately one watt in either of the two strongest lines (4880 Å and 5145 Å). Anticipated overall improvement in sensitivity resulting from the increase in power, advantage due to the ν^4 scattering law, enhanced photomultiplier response and grating efficiency is approximately 100.

B. Spectrograph

Raman scattered light is analyzed with a Spex model 1400 tandem grating spectrometer. This instrument virtually climinates internal scattering of parasitic exciting light (suppression of at least 10^7 at 5 Å from exciting line with 50 micron slits).

C. Phototube

The photomultiplier is an ITT "Startracker" FW 130 with a slit-shaped photocathode matched to the spectrometer exit slit. The tube is operated at dry ice temperature and produces a dark current of only one to five counts per second. As a result, the limiting noise is the fluctuation in the signal itself rather than the dark current, even for very weak signals.

D. Signal Analysis

The photomultiplier output pulses are processed by a pulse amplifier and single channel analyzer. The single channel analyzer output is then converted to an analog signal by a ratemeter whose output is recorded on a strip chart recorder. This method of signal processing has been found to give maximum discrimination against spurious sources of noise such as dynode emission, tube breakdown, cosmic events, etc.

E. Sample Thermostats

Since most of the experiments must be performed under rather special and carefully controlled temperature conditions, we have built a group of special ovens and cryostats for the individual experiments. These include a large double oven capable of operation up to 800° C, and a very stable nitrogen cryostat for operation near the ferroelectric transition temperature of KDP at 123°K. A commercial helium cold-finger dewar (Hoffman-Pauli) is also in use and has been modified to permit operation over a large range of temperatures from liquid helium to above room temperature.

II. STRONTIUM TITANATE

Preliminary temperature-dependent Raman measurements of strontium titanate were discussed briefly in our preceding report. As we mentioned then, the room temperature spectrum is so intense and the peak at 78 cm^{-1} so well defined that we concluded that the observed spectrum must be at least in part of first order (see Fig. 1). Subsequent temperature vs. intensity measurements of the 78 cm^{-1}

line failed to confirm this analysis, however, and we are at present unable to state that any part of the room temperature spectrum is definitely of first order.

During the temperature dependent runs, we found an unexpected feature in the spectrum - a broad "line" whose Raman frequency changes with temperature as $\omega^2 \propto (T - T_c)$(this result has been published in Reference 1).

Below the cubic to tetragonal transition at 110°K, three sharp lines appear in the Raman spectrum at 44, 142 and 446 cm^{-1}. Although these sharp lines have also been reported by others, their origin has never been explained.

We have recently obtained evidence which indicates that these lines arise within the domain walls separating regions with different orientations of the principal symmetry axis. Although in the "normal" crystal each ion occupies a center of symmetry so that first order Raman scattering is forbidden, the inhomogeneous strain within the domain walls breaks the symmetry locally and permits Raman activity.

An alternative symmetry breaking technique was recently demonstrated by Fleury and Worlock[2]. Application of a strong electric field displaces the charged ions from their normal equilibrium positions to new positions lacking inversion symmetry. When the field is applied those lattice modes which are normally infrared active but not Raman active, will exhibit Raman activity due to the lowering of the symmetry.

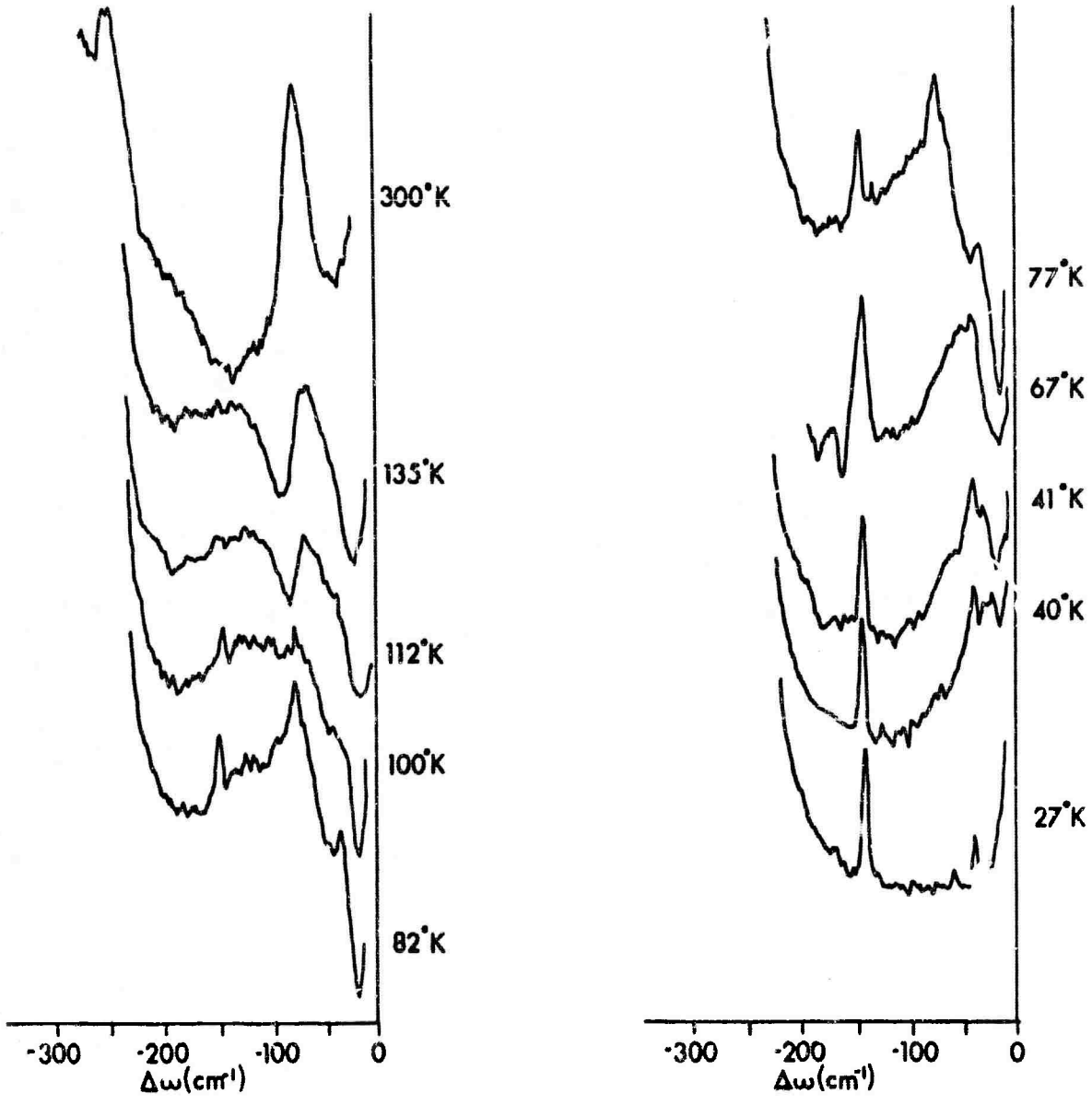

FIGURE 1 : STRONTIUM TITANATE - TEMPERATURE DEPENDENT RAMAN SPECTRUM. (0 - 300 cm^{-1})

Because of the fundamental role played by infrared active lattice modes in the perovskite phase transitions, this technique is of particular value in the present study and we are also applying it to the study of strontium titanate.

III. QUARTZ

In 1956 Yakovlev et al studied the total light scattered by quartz as a function of temperature.[3] They observed that at the α-β phase transition temperature, the intensity of the scattered light increased by a factor of 10^4 over the room temperature level. This anomalous increase in scattered light was termed opalescence, since it resembled the effect observed in liquids at the liquid-vapor critical point. It is our aim to study the spectral components of the scattered light using Raman and Brillouin scattering techniques.

Quartz undergoes a phase transition at 573°C from the low temperature α phase with point symmetry D_3 to the high temperature β phase with symmetry D_6. In the low temperature phase there are four totally symmetric Raman active modes of species A_1 and eight doubly degenerate Raman and infrared active modes of species E. The four A_1 modes have been previously assigned as 207, 355, 466 and 1081 cm^{-1}. By selecting the proper polarization of the incident and scattered light, the A_1 and E modes can be separated. In addition to the four A_1 lines mentioned above, an unexpected weak line at 147 cm^{-1} is observed.

Group theoretical analysis indicates that in the transition to β quartz, the eight doubly degenerate E modes should remain Raman active with the same polarizations. Three of the A_1 modes should go into Raman inactive modes, and one A_1 mode should be present in the beta phase.

Figure 2 shows part of the A_1 spectrum at five different temperatures (the topmost trace is in the beta phase). The most striking result is the rapid increase in intensity of the weak 147 cm^{-1} line and its corresponding decrease in frequency as the sample approaches its transition temperature. The 147 cm^{-1} line is not present in the beta phase. The 207 cm^{-1} broadens and shifts toward lower frequencies, but its frequency does not reach zero, and it is still present in the beta phase as a broad band centered at 162 cm^{-1}. The 466 cm^{-1} is still present in the beta phase and has shifted to 459 cm^{-1}. The 355 cm^{-1} and 1081 cm^{-1} lines decrease continuously in intensity with little change in frequency and are not present in the beta phase.

The above results contradict earlier experimental and theoretical work. Narayanaswamy[4] studied the temperature dependent Raman spectrum of quartz in 1947 and found that the frequency of the 207 cm^{-1} line shows a strong variation with temperature and as the transition temperature is approached it moves toward the Rayleigh line, broadens and disappears completely in the beta phase. In the theoretical analysis of Kleinman and Spitzer, it was found that the displacements of the atoms necessary to transform alpha quartz into beta quartz were most closely represented by the motions associated with the 207 cm^{-1} A_1 mode.[5] Narayanaswamy's experiment supported their conclusion.

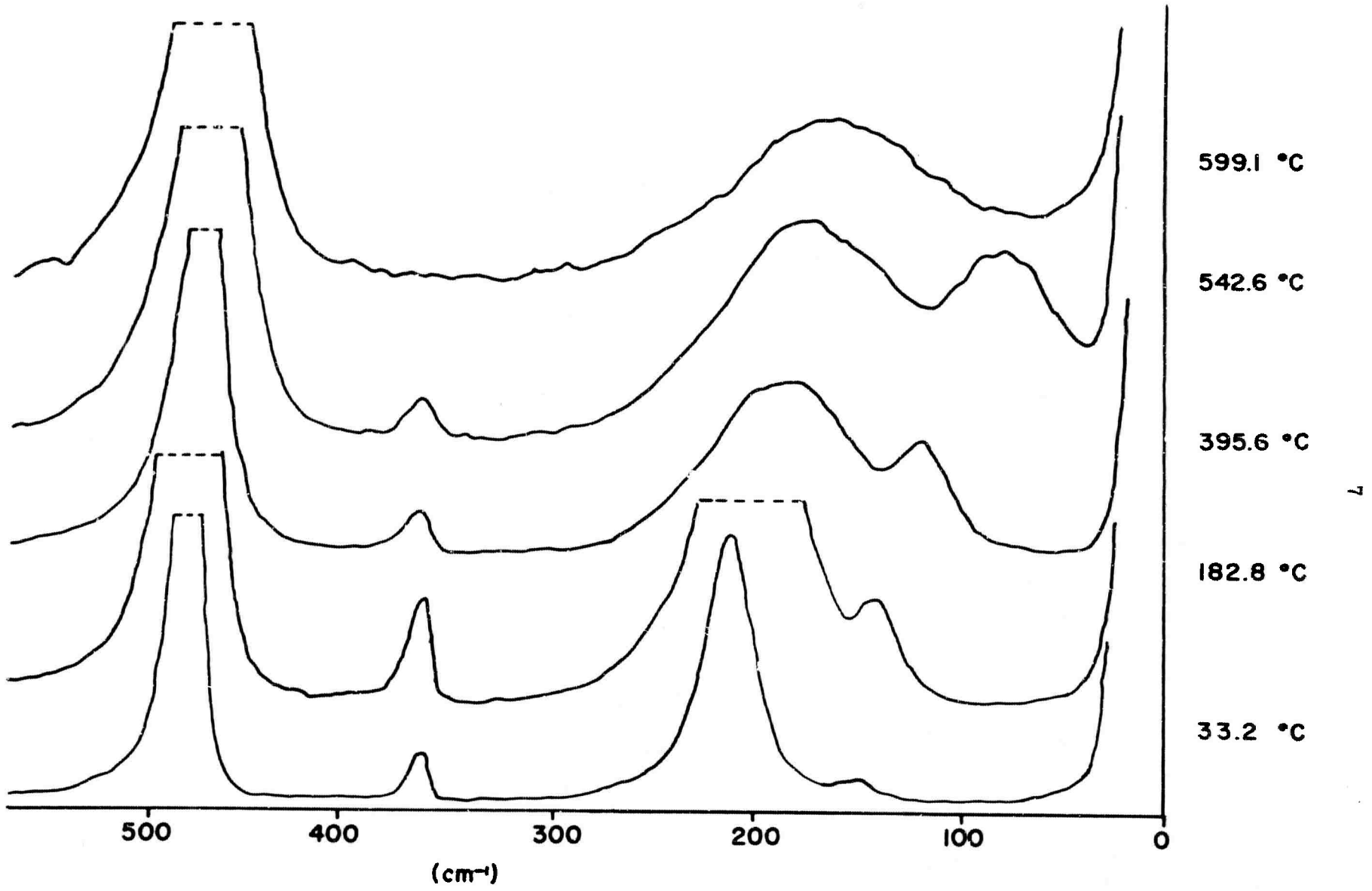

FIGURE 2. TEMPERATURE DEPENDENT RAMAN SPECTRA OF QUARTZ", 0-550 Cm^{-1}. UPPER TRACE IN BETA PHASE.

Our experiment shows five A_1 modes in the alpha phase and two in the beta phase, and the 147 cm^{-1} being the mode whose frequency goes to zero as the phase transition is approached. Either the present assignments of the A_1 modes, or the accepted structure which, via group theory, predicts the allowed modes, must be in error. The assertion that the 147 cm^{-1} line arises from a second order effect would contradict its apparently fundamental role in the phase transition and cannot in any case resolve the difficulty in the beta phase resulting from the persistence of both the 466 and the 207 cm^{-1} lines.

Presently there is no consistent explanation of the above observations. An attempt to create a phenomenological model which explains the basic results has been included in our publication reporting the above experimental results.[6]

IV. CALCIUM TUNGSTATE

Work has been completed on the analysis of the $CaWO_4$ Raman spectrum. This work, initiated as a Raman study of laser host crystals, agrees in detail with the recently published work of Porto and Scott.[7] This research was most useful in clarifying Raman selection rules and serving as a relatively easy, but not trivial, example of first order Raman scattering. Through the use of group theoretical analysis many of the lines could be attributed to certain lattice modes and internal tungstate ion vibrations. This analysis has also contributed to our present work on KH_2PO_4.

V. POTASSIUM DIHYDROGEN PHOSPHATE (KDP)

KDP undergoes a ferroelectric phase transition at 123°K. Brillouin scattering studies of this transition have been in progress for some time in this laboratory.

It is now widely accepted that displacive ferroelectric phase transitions (and perhaps many other crystalline phase transitions as well) result from an instability in the lattice dynamics and that the transition can be very effectively studied by observing the frequencies of the q = 0 lattice vibrations as a function of temperature.

Cochran[8] has considered KDP in some detail and estimates that the "ferroelectric" lattice mode will have a frequency of about 85 cm^{-1} at room temperature, and decrease to about 14 cm^{-1} at the transition (123°K).

We have completed preliminary temperature dependent Raman measurements of KDP and see an indication of a heavily damped mode of frequency less than 100 cm^{-1}. The effect, if real, is extremely weak giving signals on the order of the dark current (1 to 5 counts/sec). Further experiments will be postponed pending the arrival of the new argon ion laser.

VI. PROGRAM FOR THE NEXT PERIOD

The strontium titanate experiments will be stressed in an effort to complete the investigation of the domain wall symmetry breaking effect. Absolute calibration of the Raman spectrometer

is in progress and will be followed by measurements of absolute Raman cross sections for several crystals.

A cooperative program has been initiated with Dr. C. K. Jen and coworkers of the J. H. U. Applied Physics Laboratory to study color centers in crystals by Raman spectroscopy. Initial efforts will involve V_k centers in alkali halides. Crystal samples will be prepared at A. P. L. and mounted in a special dewar. They will then be brought here for x-ray irradiation and Raman analysis.

With the installation of the new argon ion laser, we also will be able to continue Raman measurements on quartz well up into the high temperature (β) phase.

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